ENGINEERING, ECONOMIC, AND POLLUTION CONTROL ASSESSMENT OF THE MEYERS' PROCESS FOR REMOVAL OF PYRITIC SULFUR FROM COAL

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INTRODUCTION

Combustion of coal for heat, steam, and electrical power generation is by far the largest single source of atmospheric sulfur dioxide pollution in the United States; it currently accounts for about two-thirds of the total sulfur oxide emissions. The Federal government has established Standards of Performance for New Stationary Sources (1). These standards limit the discharge of sulfur dioxide into the atmosphere to 1.2 pounds per million Btu's of heat input for solid fossil fuel combustion operations generating more than 250 million Btu's per hour. This emission limit corresponds to a maximum sulfur content restriction of 0.6 - 0.8% for most Eastern coals. However, coal for utility consumption averages about 2.5 - 3.0% sulfur. The Meyers' Process presents a new and potentially low cost approach to meeting a significant portion of the requirement for low sulfur coal.
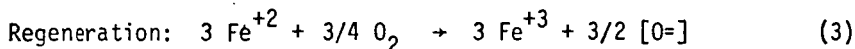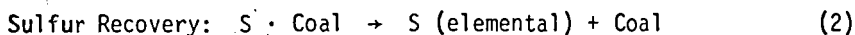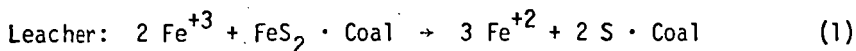
The Meyers' Process, initially developed by TRW, Inc., utilizes a simple chemical leaching method to remove iron pyrite from the coal matrix. The process is presently at a bench-scale development phase, under sponsorship of the Control Systems Division, Office of Research and Monitoring, Environmental Protection Agency, with an objective of obtaining all data necessary for the design and operation of a pilot or, eventually, a demonstration plant.

This paper presents the results of preliminary commercial scale process engineering and economic assessments of the Meyers' Process and describes the potential of the process for converting current steam coal production to a sulfur level consistent with Federal regulations for controlling sulfur dioxide emissions from stationary sources.

GENERAL PROCESS CHEMISTRY

The basis for the Meyers' Process for the removal of inorganic (pyritic) sulfur from coal involves contacting the iron pyrite in the coal with an aqueous ferric sulfate solution and oxidizing the pyritic sulfur to elemental sulfur. The free sulfur can then be removed from the coal matrix by solvent extraction or various other processing methods (e.g., steam or vacuum vaporization), and the oxidizing agent can be regenerated (e.g., by air oxidation) and recycled.

The chemistry associated with the process can be illustrated for the individual process operations as follows:

$$\text{Leacher:} \quad 2\ Fe^{+3} + FeS_2 \cdot Coal \rightarrow 3\ Fe^{+2} + 2\ S \cdot Coal \tag{1}$$

$$\text{Sulfur Recovery:} \quad S \cdot Coal \rightarrow S\ (elemental) + Coal \tag{2}$$

$$\text{Regeneration:} \quad 3\ Fe^{+2} + 3/4\ O_2 \rightarrow 3\ Fe^{+3} + 3/2\ [O=] \tag{3}$$

In addition, about 60 percent of the pyritic sulfur content of the coal has been found to oxidize to sulfate which dissolves in the aqueous leaching solution. The postulated chemistry for sulfate formation during the pyrite leaching is:

$$FeS_2 + 14\ Fe^{+3} + 8\ H_2O \rightarrow 15\ Fe^{+2} + 2\ SO_4^= + 16\ H^+ \tag{4}$$
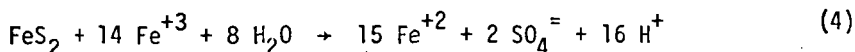
The unique aspect of this process is that iron is used to remove iron. Also, the utilization of an iron sulfate leaching system eliminates the possibility of depositing extraneous chemicals on the coal (both iron and sulfate are present in raw coal). Since the leaching solution can be regenerated, the process, when viewed as a unit, removes iron pyrite from coal by utilizing air (or oxygen) as a raw material and produces elemental sulfur and iron sulfates and/or iron oxides as products.

PROCESS ENGINEERING

The proposed process design is based mainly on the results of laboratory and bench-scale experimentation studies dealing with Lower Kittanning coal. The base case processing rate was selected at 100 tons of coal per hour (equivalent to a 250 MW utility output) with approximately 3.2 tons per hour of pyritic sulfur removed from the coal.

A block diagram showing the processing steps currently envisioned for the removal of pyritic sulfur from coal is presented in Figure 1. The process contains four main sections.

- Pyrite leaching with ferric sulfate solution.
- Regeneration of the ferric sulfate leach solution.
- Coal washing with water.
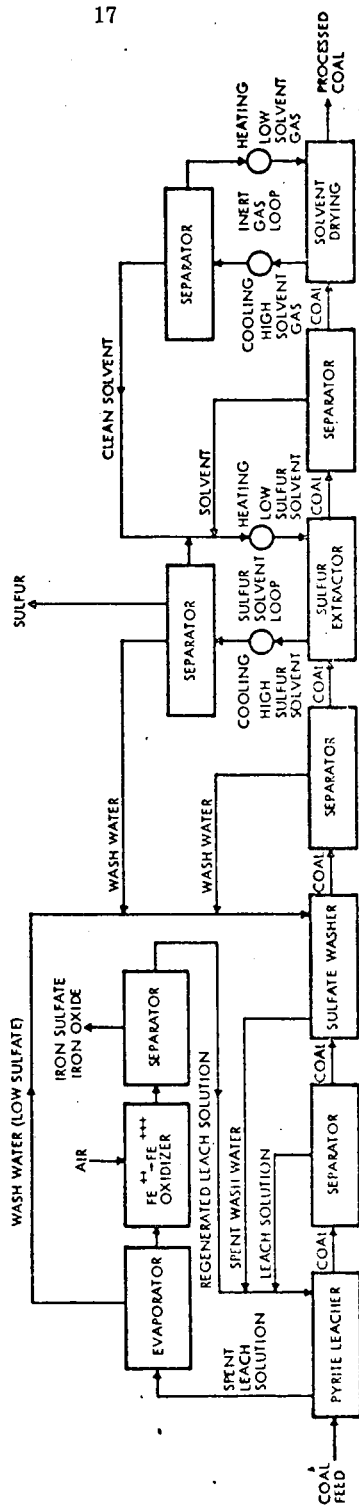- Sulfur recovery by solvent extraction and coal drying.

Figure 1. Pyritic sulfur removal process block diagram.

Pyrite Leaching

Based on experimental results, a countercurrent leach step appears desirable; freshly regenerated ferric ion is first contacted with coal nearly depleted in pyrite. Preliminary experimental results indicate that neither ferrous ion nor sulfate ion buildup has a significantly adverse effect on the reaction; thus, the nearly spent leach solution should still be actively attacking pyrite on the freshly introduced coal stream. With fresh coal introduced at the beginning of the leach, there is probably sufficient pyrite near the surface of the coal particle so that no effect on the rate of etching of the pyrite surface is produced by the high ferrous ion concentration. It is believed that toward the end of the leach step, the rate of reaction is controlled mainly by counterdiffusion of ferric ion into and ferrous ion out of the pores in the coal particles; the rate is thereby benefited by high ferric and low ferrous ion concentrations in the leach solution. If this model of the leach step is correct, then the leacher requires little bulk mixing. Equipment which slowly moves coal countercurrently through a slowly flowing stream of leach solution will be highly effective as a leach reactor.

Three coal particle sizes (-1/4 inch, -14 mesh, and -100 mesh) have been studied during the present experimental work. The results indicate that pyritic sulfur removal is possible with all of the above coal particle sizes. The process design provides for a coal leach residence time of four hours. The leacher design temperature is at or near the atmospheric boiling point of the solution (about 100°C) and the design pressure is atmospheric.

It is anticipated from current experimental results that the reaction of ferric ion with pyrite in coal will yield a $SO_4^=/S$ reaction product ratio of about 1.5/1. A leach solution of approximately 7500 GPM of 0.5 M ferric ion concentration (100% excess of ferric ion required for complete reaction) with little ferrous ion content or acidity is the nominal design feed to the leacher.

The coal discharging from the pyrite leacher is separated from the bulk of the leach solution and conveyed to a water wash system. It is probable that the separation can be accomplished with simple moving-belt screen filters since surface fluids are readily removed during the next processing step. (Even if powerful centrifuges were employed, fluids would not be driven from one-half of the coal pores which are oriented toward or into the induced centrifugal force field.) The leach solution recovered in the separator is recycled back to the pyrite leacher.

Regeneration of the Pyrite Leach Solution

Spent leach solution from the pyrite reactor will contain unreacted ferric ion, ferrous ion, by-product and recycled sulfate ion, recycled and spent wash water, acid produced by the sulfur and sulfate reactions, numerous minor elements, and possibly some water soluble organic compounds leached from the coal. Regeneration of the leach solution includes the separation of a low ion content wash water for return to the wash section, the air oxidation of ferrous ion to ferric ion, and the separation of ferrous or ferric sulfate and iron oxide in the quantities produced during the leach step.

Regeneration of ferric ion from an aqueous solution of acidic ferrous ion is readily accomplished by oxidation with air. As shown in Figure 1, the regeneration may be carried out in equipment separate from the pyrite leach reactor. This arrangement offers the greatest opportunity for using technology developed independently of the coal leaching. (Regeneration of coal leach solution has much in common with treatment of spent pickle solutions from descaling of iron or steel. Oxidation of ferrous ion to ferric ion is receiving the greatest attention in hydrochloric acid pickling where oxidation of ferrous chloride to ferric chloride precedes hydrolysis and acid recovery.)

Water Washing

Water washing the coal leaving the pyrite leacher is necessary to remove residual leach solution. (Leach solution not washed from the coal will deposit sulfate on the coal during drying and reduce the extraction efficiency.) From bench scale experience, it has been found that drained Lower Kittanning coal retains about 20% w/w of the ferric sulfate leach solution. (These weights were similar for either the -1/4 inch or the -14 mesh samples.) The removal of leach solution from the pores of the coal particles is probably a diffusion controlled process and, if this is the case, could ideally be carried out in a countercurrent washer with long residence time. It is reasonable to predict that a washing time of 5 to 50% of the leaching time, and wash water requirements in the range of one-half to one pound water per pound of coal would be capable of removing substantially all of the residual leach solution from the coal. The spent wash water is pumped to the pyrite leacher, and the water on the coal discharging from the water washer is drained on a moving-belt screen filter. (Bench scale experience indicates drained Lower Kittanning retains about 15% w/w wash water based on dry coal weight.)

Sulfur Extraction and Coal Drying

The coal exiting the washer still contains elemental sulfur formed from pyrite in the coal particles during the leach reaction. The proposed process shown in Figure 1 uses a dissolvent (e.g., aromatic or aliphatic hydrocarbon) to extract the elemental sulfur from the coal. Residual wash water is also displaced from the coal pores during the sulfur extraction. Toluene has been used for extraction in laboratory and bench scale experimental work, but any low priced, convenient solvent could be substituted.

The hot, sulfur-rich solvent exiting the sulfur extractor is cooled to cause sulfur to precipitate from solution, filtered to recover the sulfur, and separated from any immissible water. The low sulfur content solvent is reheated and recycled to the sulfur extractor.

The coal exiting the sulfur extractor is conveyed to a solvent dryer where any residual sulfur solvent is removed. A heated inert gas is used to evaporate the solvent from the coal and carry it to a condenser where the solvent is condensed, separated from the inert gas, and recycled to the sulfur extractor. The dry processed coal is allowed to cool and is then conveyed to storage.

Several alternative methods for removing and recovering elemental sulfur from coal have been assessed in preliminary evaluations. One method involves heating the wet, water-washed coal to molten sulfur temperature (i.e., 250°F) under pressure (15 to 50 psig) and then rapidly depressurizing the coal to cause steam to be formed in the pores. It is postulated that the steam venting from the pores will drive the liquid sulfur droplets from the pores and into the steam condensation equipment. If such a process step is found to be oper-able, the solvent extraction and solvent drying steps can be eliminated, and steam stripping the sulfur byproduct to remove solvent would be unnecessary.

Other processing methods which have been proposed as alternatives to the sulfur solvent extraction include: 1) melting and displacement of the sulfur in the coal by superheated water (i.e., 50 psig, 300°F) and 2) vaporization of the elemental sulfur by a heated inert carrier gas (e.g., nitrogen), followed by cooling of the carrier gas and condensation and separation of the sulfur.

PROCESS ECONOMICS

Capital and operating costs have been estimated by TRW for a Meyers' pro-cessing plant capable of handling 100 tons of coal per hour (sufficient to feed a 250 MW coal fired power plant). Table 1 presents a summary of the capital and processing costs. The estimated overall processing cost for the baseline pyritic sulfur removal process is $1.95 per ton of coal (8¢ per MM Btu). The capital cost for the plant is estimated to be $4 million. As the process is further developed from the bench-scale work these cost figures will change and thus the process economics will be accordingly updated and independently examined.

The coal processing cost is based on 10-year straight line depreciation of the capital plus 10 percent of capital committed annually for maintenance, taxes and insurance. The direct labor costs correspond to 41 operators including shift foreman and plant foreman. A weekly cost per operator was estimated at $200 plus 25 percent payroll burden for fringe benefits. No credit was allowed for the process products: elemental sulfur, iron oxide and iron sulfate. Also no sulfur solvent was assumed retained in the processed coal. (For 0.1% w/w solvent retention in the processed coal, the processing cost increases by approxi-mately 6¢/ton coal.)

The capital cost estimate was developed by estimating major equipment costs and applying installation factors. The capital includes equipment costs for a 25 ft. diameter x 100 ft. long stainless steel-clad kiln-type leach vessel, separators, washer, sulfur extractor, solvent dryer and leach solution regene-ration (factored from the leacher cost), heat exchangers (based on calculated surface), pumps and air blower (calculated from estimated horsepower). Each equipment cost was multiplied by a factor to cover field material and labor, engineering, etc.; these installed costs were than added to give the total capital cost.

The costs do not include those for a coal preparation plant because they may already be included in utility operating costs. For instance, if an elec-tric generating facility utilizes a pulverized coal fired boiler, much of the coal preparation requirement may already be in operation. Also if a utility

Table 1

Meyers' Process Economics

Capital Investment	$MM
Pyrite Leach System	1.5
Leach Solution Regeneration System	1.0
Water Wash Unit	0.5
Sulfur Extractor and Coal Dryer	1.0
Total Capital	4.0

Processing Cost	$/Ton Coal
Utilities	0.35
Labor	0.60
Maintenance, Taxes and Insurance	0.50
Depreciation	0.50
Total Processing Cost	1.95

is currently purchasing coal which has been treated in a coal preparation plant to remove rock, etc., additional coal preparation costs may not be necessary, as preliminary experimental results have demonstrated the Meyers' process capable of handling large coal particle sizes (e.g., -1/4 inch).

No provision was included for a return on investment charge for a Meyers' process plant, since the justification for plant installation would be compliance with pollution control regulations and/or the cost incentives associated with utilizing low cost high sulfur coal.

POLLUTION CONTROL

The Meyers' process for the extraction of pyritic sulfur will have essentially 100% application to new and existing coal combustion activities. Since the process produces a cleaned fuel from raw coal, it can be installed at either a combustion site or a mine-mouth location.

The present test work has shown the Meyers' process to be capable of achieving nearly total removal of pyritic sulfur from coal. The pyrite reductions obtained have not indicated any variations due to the rank of the coal, coal region, or coal bed. At an estimated operating cost of $1.95 per ton of coal processed, the pyritic sulfur removal process has excellent economic potential for use either alone or in conjunction with an organic sulfur control technique. The two processes could present a unified overall technique for the total elimination of sulfur dioxide emissions from combustion of the processed coal. Evaluations indicate that use of the pyritic sulfur removal process as the sole SO_2 control technique can result in a considerable impact upon sulfur dioxide emission control.

Coals which typically contain a majority of their sulfur content in a pyritic form are found in the coal mining regions of the Eastern United States (Appalachian Basin). These coal regions are important because the Appalachian Basin contains one-third of the known remaining bituminous coal reserves of the United States and one-half of the estimated total remaining resources east of the Mississippi River, representing a total reserve value of over 280 billion tons of coal (2). The Appalachian Basin also supplies 60% of the total U. S. demand for bituminous coal (3).

The sulfur content of the steam coals in the Eastern coal mining regions has been extensively examined by the U. S. Department of the Interior's Bureau of Mines (4). Consideration of the sulfur content of the Appalachian coals in conjunction with coal bed characteristics from the 1971 edition of the Keystone Coal Industry Manual (3) indicates that less than 10% of the coal mined for utility use in the Appalachian Basin is capable of meeting the sulfur dioxide emission standard of no greater than 1.2 pounds of SO_2 emitted per million Btu's of input energy, as shown in Figure 2. Figure 2 also illustrates that the application of the Meyers' process for pyritic sulfur removal at 95% efficiency can increase the quantity of Appalachian coal capable of meeting the performance standard by a factor of four.
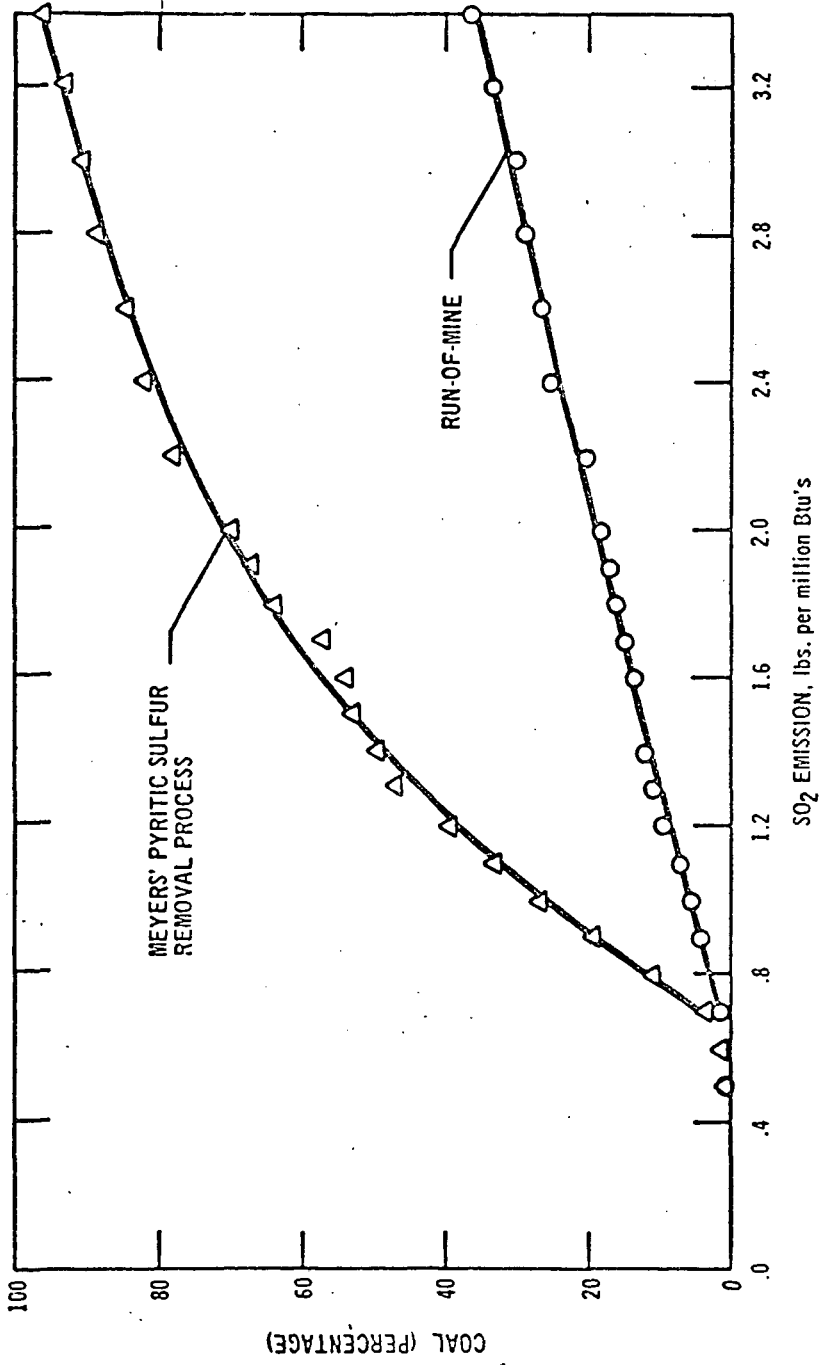
Figure 2. Sulfur Dioxide Emission Characteristics of Appalachian Basin Coal

The impact of the Meyers' process on pollution abatement is even more evident when consideration is given to the utility coals mined in the Pennsylvania bituminous and Maryland state regions. Figure 3 shows that 23% of the as-mined utility coal in Maryland is capable of meeting the new SO_2 emission standards, while 76% of the Maryland coal will be able to meet the standard after application of the pyritic sulfur removal process.

Figure 4 shows that, in Pennsylvania, a ten-fold increase in useable steam coal quantities above the 5% as-mined bituminous coal which meets the New Source Performance Standards is achieved upon application of the Meyers' Process.

CONCLUSION

In active experimentation funded by the Environmental Protection Agency, TRW, Inc., has developed a bench-scale method for leaching pyritic sulfur from coal. In the Meyers' Process, pyritic sulfur is removed by ferric sulfate reaction with the pyrite in coal and recoverable elemental sulfur and dissolved sulfate species are generated. Reaction conditions of 100°C and atmospheric pressure are envisioned, with 95-100% removal of pyritic sulfur a reality. Although the projected operating cost for application of this pyritic sulfur leaching technique may make the process attractive for use in combination with an independent, economically low-cost method for organic sulfur removal, the Meyers' process for pyritic sulfur removal has the potential for widespread production of a clean fuel capable of meeting Standards of Performance for New Stationary Sources.
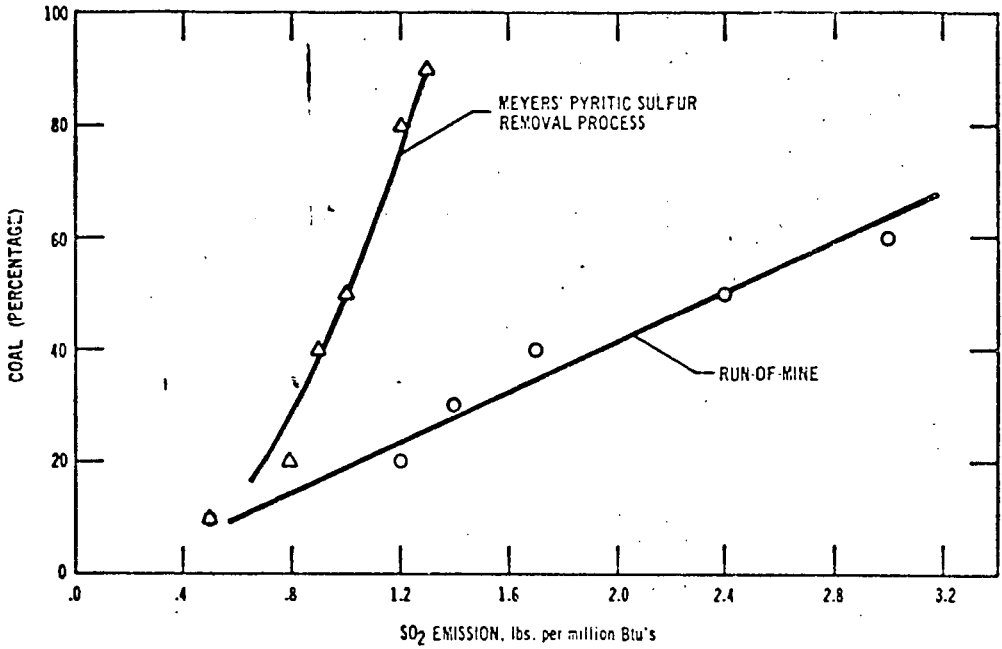
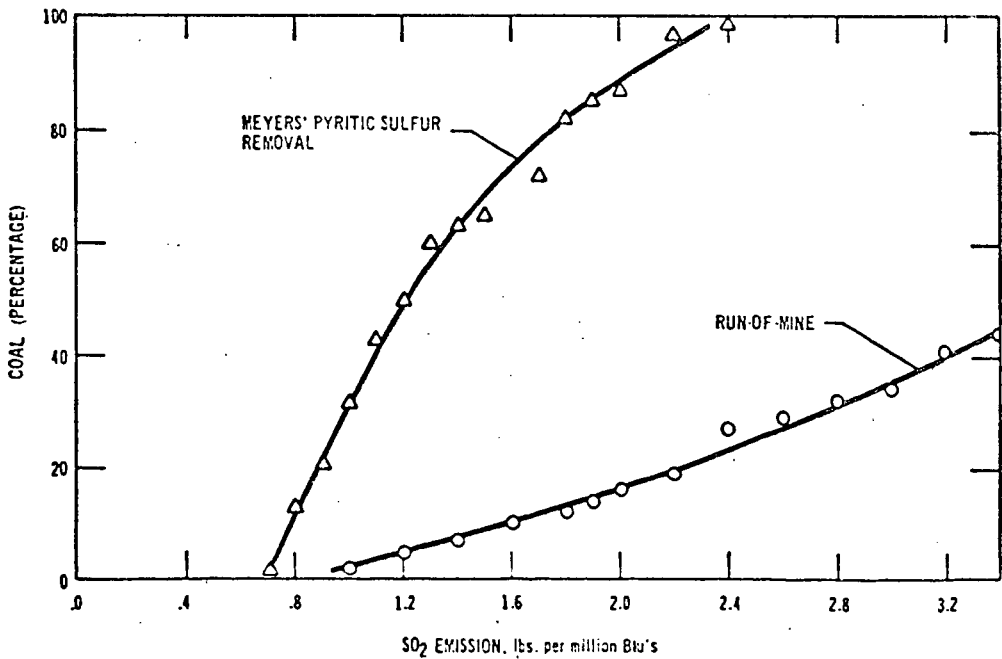Figure 3. Sulfur Dioxide Emission Characteristics of Maryland Coal.

Figure 4. Sulfur Dioxide Emission Characteristics of Pennsylvanian Bituminous Coal.

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